

Sorption of vinclozolin and atrazine on four geosorbents

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Abstract: The objectives of this study were to evaluate the magnitude and kinetics of vinclozolin and atrazine sorption on one surface soil and three freshwater sediments using batch and column techniques. Data from miscible displacement column studies were analyzed using a two-domain, first-order mass transfer model to obtain the equilibrium sorption constant (K) and the first-order desorption rate coefficient (k_2). In the two-domain conceptualization and mathematical model, sorption is assumed to be instantaneous (and therefore at equilibrium) in the first domain, and kinetically controlled (modeled as a first-order reaction) in the second domain. $^3\text{H}_2\text{O}$ used as a conservative tracer to characterize column hydrodynamics yielded breakthrough curves (BTCs) that were all symmetric and the data were described well by the advective-dispersive local equilibrium solute-transport model, thus indicating hydrodynamic equilibrium during transport for the column systems. However, vinclozolin and atrazine BTCs exhibited the 'tailing' that is characteristic of non-equilibrium sorption during solute transport. The equilibrium model provided poor fits for all of the vinclozolin and atrazine data except for the least-sorbing geosorbent and atrazine where BTC symmetry was high. However, when slow sorption kinetics were accounted for, the two-domain model simulations provided good descriptions of the experimental data.

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1 INTRODUCTION

Soil and sediment are important environmental sinks for atrazine and vinclozolin. Accordingly, the magnitude and kinetics of sorption of these pesticides are important factors in determining their environmental fate and the potential for biota exposure. The objectives of this study were to evaluate the relationships between the equilibrium sorption constant (K), the first-order desorption rate coefficient (k_2), and geosorbent organic carbon content. Data from miscible displacement studies using soil columns were analyzed using a two-domain, or bicontinuum, first-order mass transfer model to obtain K and k_2 .

2 MATERIALS AND METHODS

2.1 Materials

The vinclozolin and atrazine used as solutes in these experiments were >99% pure (Crescent Chemical Co, Hauppauge, NY). All solvents (Fisher Scientific, Pittsburgh, PA) used in the HPLC analyses were HPLC grade. Tritiated water, $^3\text{H}_2\text{O}$ (Sigma Chemical Co, St Louis, MO), was used as a non-sorbing tracer to characterize hydrodynamic dispersion in the column systems. A preparatory-scale liquid chromatography column (Kontes, Vineland, NJ) of 2.54 cm

ID. with adjustable bed length was dry-packed with the <250 μm fraction of the Eustis soil or one of the three sediments. The Eustis soil was collected from the top 10 cm of the soil surface near Gainesville, FL; the Oconee sediment was collected from the Oconee river in Athens, GA; the Hayes sediment was collected from a small man-made impoundment (Hayes Lake) in Athens, GA; and the Lightwood sediment was collected from Lightwood Log Creek, a small stream that feeds into the Lake Hartwell Reservoir in Northeast GA. All of the geosorbents were air-dried and then sieved prior to use. Pertinent geosorbent and column information is contained in Table 1.

2.2 Apparatus and technique

The experimental apparatus and methodology used in the batch equilibrium and column miscible displacement experiments were similar to those used previously by the author.^{1,2} In the batch equilibrium studies, from one to six grams of geosorbent were weighed into 15-ml centrifuge tubes, known volumes of 0.01 M calcium chloride solution were added to thoroughly wet the geosorbents, and then aliquots of the pesticides in 0.01 M calcium chloride were added to obtain the initial pesticide concentrations (C_0 , μM). The C_0 values ranged from 0.05 to 2.0 μM for

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Table 1. Parameters for geosorbents and columns used in batch sorption and miscible displacement studies

Parameter	Geosorbent			
	Oconee	Hayes	Eustis	Lightwood
Organic carbon (%)	1.02	0.66	0.61	0.12
pH	5.5	4.7	5.1	5.8
Sand (%)	65.4	71.1	91.8	83.3
Silt (%)	25.3	17.9	5.0	9.8
Clay (%)	9.3	10.9	3.2	6.9
Vol water content (cm ³ cm ⁻³)	0.513	0.449	0.376	0.443
Bulk density (gcm ⁻³)	1.290	1.461	1.654	1.502
Length (cm)	5.4	6.0	5.2	6.0
Pore water velocity (cm h ⁻¹)	39.2	31.6	37.8	32.8
Peclet number	260	69	86	77

vinclozolin and from 0.25 to 50.0 µM for atrazine. The centrifuge tubes were then gently agitated for 8 h followed by centrifugation at 800 RCF for 30 min. Aliquots of the supernatant were then removed for analysis by HPLC.

In the column systems, the packed soil/sediment column was oriented vertically and connected to two syringe pumps through an inert valve which allowed switching between the eluting phases delivered by the pumps to the column. One pump contained an eluting phase of 0.01 M calcium chloride and the other contained 0.01 M calcium chloride and vinclozolin, atrazine or ³H₂O. Initially, the column was wetted slowly from the bottom with calcium chloride solution until the system was completely saturated. Break-through curves (BTCs) were then conducted by introducing a pulse of the pesticide in calcium chloride solution into the column and monitoring the column effluent until the pesticide effluent concentration, *C*, approached the influent concentration, *C*₀, ie *C*/*C*₀ = 1. This solution was then displaced from the column with calcium chloride solution until *C*/*C*₀ = 0 was approached. Vinclozolin and atrazine concentrations in the column effluents were determined by collecting and analyzing fractions using HPLC. Column effluent fractions collected from the ³H₂O BTCs used to characterize column hydrodynamics were analysed by liquid scintillation counting.

2.3 Data analysis

A two-domain, or bi-continuum, first-order mass transfer model was used to analyze the data generated in the BTC experiments. This model has been used with considerable success to describe solute transport through a variety of geosorbents, including soils, sediments, and aquifer materials.^{3,4} For the bi-continuum model, sorption in domain 1 is assumed to be instantaneous, and sorption in domain 2 is rate-limited and described by first-order reversible kinetics. Sorption in both domains is assumed to follow linear sorption isotherms. Five parameters (*T*₀, *P*, *R*, *β*, *ω*) are required to run the bi-continuum model. The size of the solute input pulse expressed in pore volumes (*T*₀) is known from measurement. The value of the

Peclet number (*P*), which represents the dispersive-flux contribution to transport, was obtained from ³H₂O BTC data by using a non-linear, least-squares optimization program⁵ to solve the advective-dispersive local equilibrium solute-transport model. Values for the retardation factor (*R*), a measure of pesticide sorption during transport; *β*, the fraction of total pesticide retardation attributed to sorption in the instantaneous domain (domain 1); and *ω*, which represents the ratio between hydrodynamic residence time and the characteristic time of sorption, were estimated by using a non-linear, least-squares optimization program⁵ for the bi-continuum model under flux-type boundary conditions.

The linear equilibrium sorption coefficient (*K*, cm³g⁻¹), was then determined from

$$R = 1 + (\rho/\theta)K \quad (1)$$

where *ρ* is the bulk density (gcm⁻³), and *θ* is the volumetric water content (cm³cm⁻³) of the porous medium. Values for the first-order desorption rate coefficient, *k*₂(h⁻¹), were calculated by substitution in eqn (2):

$$\omega = k_2(1 - \beta)RL/v \quad (2)$$

where *L* is column length (cm), *v* is the pore-water velocity (cm h⁻¹), and all other terms are as defined previously.

For the batch experiments, the pesticide solution phase concentration at equilibrium (*C*_e, µM) was plotted versus the pesticide sorbed phase concentration *S*, (nmol g⁻¹):

$$S = KC_e \quad (3)$$

and *K* determined through linear regression.

3 RESULTS AND DISCUSSION

3.1 Batch sorption studies

The batch sorption isotherms contained in Fig 1 illustrate that vinclozolin and atrazine sorption could be described by the linear sorption model (eqn (3)) over the solute concentration ranges used in these

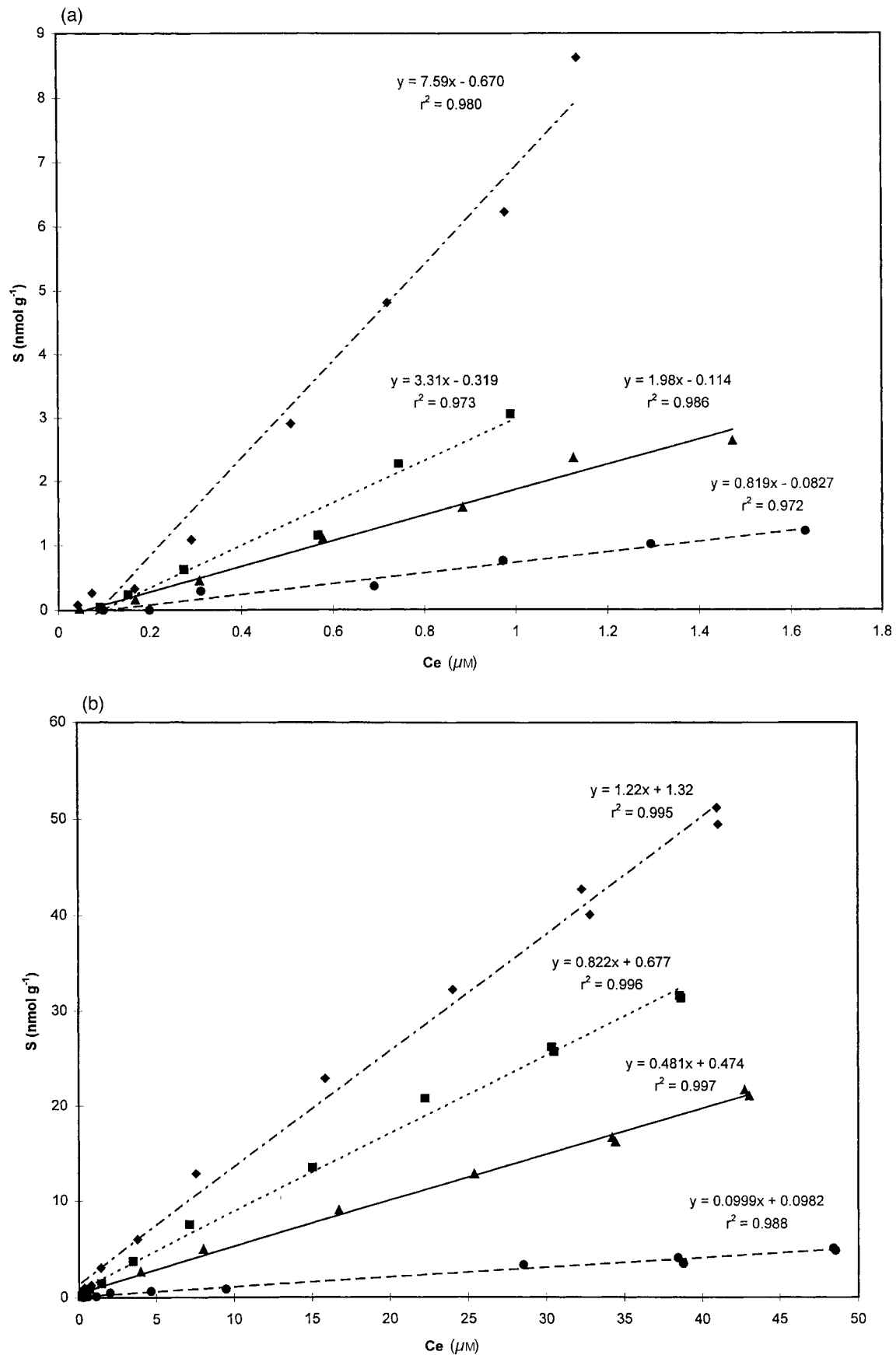


Figure 1. (a) Vinclozolin and (b) atrazine sorption isotherms for (◆) Oconee, (■) Hayes, (▲) Eustis and (●) Lightwood.

studies. Some curvature may be observed in the atrazine-Oconee and atrazine-Hayes plots (Fig 1b), but a more complex model is not justified for our

purposes. Vinclozolin was more highly sorbed than atrazine on the four geosorbents. This is consistent with the lower water-solubility of vinclozolin as

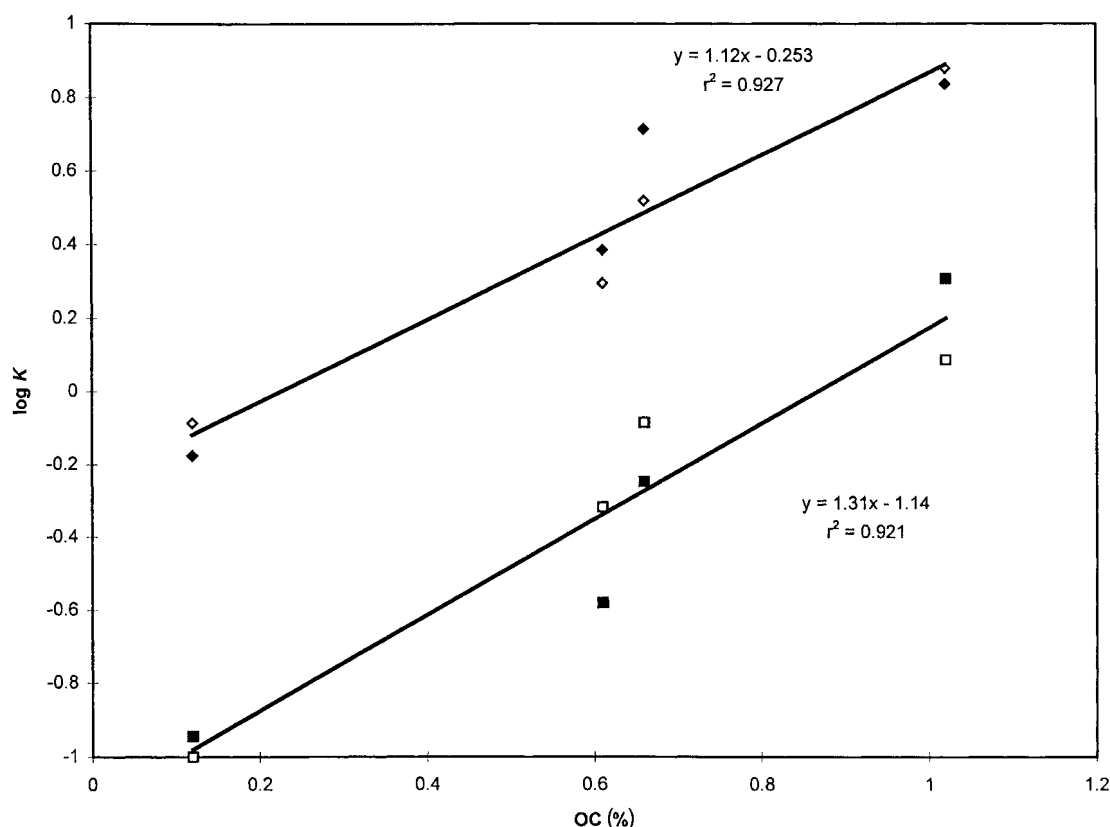


Figure 2. (◆; ◇) Vinclozolin and (■; □) atrazine sorption coefficients (K) as a function of geosorbent organic carbon content. Open symbols are batch values, closed symbols are column values.

measured in 0.01M calcium chloride in this study ($9.17\mu\text{M}$ and $174\mu\text{M}$ for vinclozolin and atrazine, respectively) and in pure water as reported in the literature⁶ ($9.09\mu\text{M}$ and $153\mu\text{M}$ for vinclozolin and atrazine, respectively). As commonly observed in sorption studies of this type, sorption increased with geosorbent organic carbon content (Fig 2; note that Fig 2 contains K values from both the batch and column studies). In addition, the slopes of the two plots in Fig 2 were not different at the 0.05 level of significance, indicating similar mechanisms of pesticide sorption by the organic carbon fraction of these geosorbents.

Although five of the eight batch K values for specific pesticide-geosorbent combinations were significantly

different from the column-derived values at the 0.05 level of significance, there was no trend in the differences and all batch and column-derived K values for specific pesticide-geosorbent combinations were within a factor of two of each other. Accordingly, the batch and column K values were averaged to yield the carbon-normalized sorption coefficients (K_{oc}) in Table 2. The K_{oc} values for each pesticide generally were within a factor of two for the four geosorbents, with only the atrazine-Eustis K_{oc} value being somewhat lower, but still within a factor of three, of the highest K_{oc} value for atrazine. The K_{oc} values for both pesticides showed an increasing trend in the order Oconee > Hayes > Lightwood > Eustis, thus indicating some small qualitative differences in the sorptivity of

Table 2. Selected sorption and transport parameters for vinclozolin and atrazine^a

Geosorbent-pesticide	R	$K_{column} (\text{cm}^3 \text{g}^{-1})$	$K_{batch} (\text{cm}^3 \text{g}^{-1})$	$k_2 (\text{h}^{-1})$	$K_{oc} (\text{cm}^3 \text{g}^{-1})$
Oconee-Vinclozolin	17.2 (16.4–18.0)	6.89 (6.57–7.25)	7.59 (6.52–8.67)	1.02 (0.940–1.12)	710
Hayes	17.91 (17.5–18.4)	5.20 (5.07–5.35)	3.31 (2.54–4.08)	1.56 (1.30–1.94)	645
Eustis	11.7 (11.3–12.1)	2.43 (2.34–2.52)	1.98 (1.75–2.21)	1.64 (1.53–1.78)	361
Lightlog	3.32 (3.04–3.59)	0.668 (0.588–0.747)	0.819 (0.659–0.979)	3.58 (2.96–4.51)	620
Oconee-Atrazine	5.77 (5.59–5.96)	2.034 (1.96–2.11)	1.22 (1.16–1.28)	3.70 (3.35–4.13)	160
Hayes	2.84 (2.73–2.95)	0.566 (0.532–0.599)	0.822 (0.787–0.856)	3.91 (3.52–4.42)	105
Eustis	2.16 (2.08–2.22)	0.263 (0.246–0.277)	0.481 (0.463–0.499)	7.34 (6.55–8.34)	61.0
Lightwood	1.40 (1.33–1.46)	0.114 (0.095–0.133)	0.0999 (0.0927–0.107)	—	89.2

^a 95% confidence limits in parentheses.

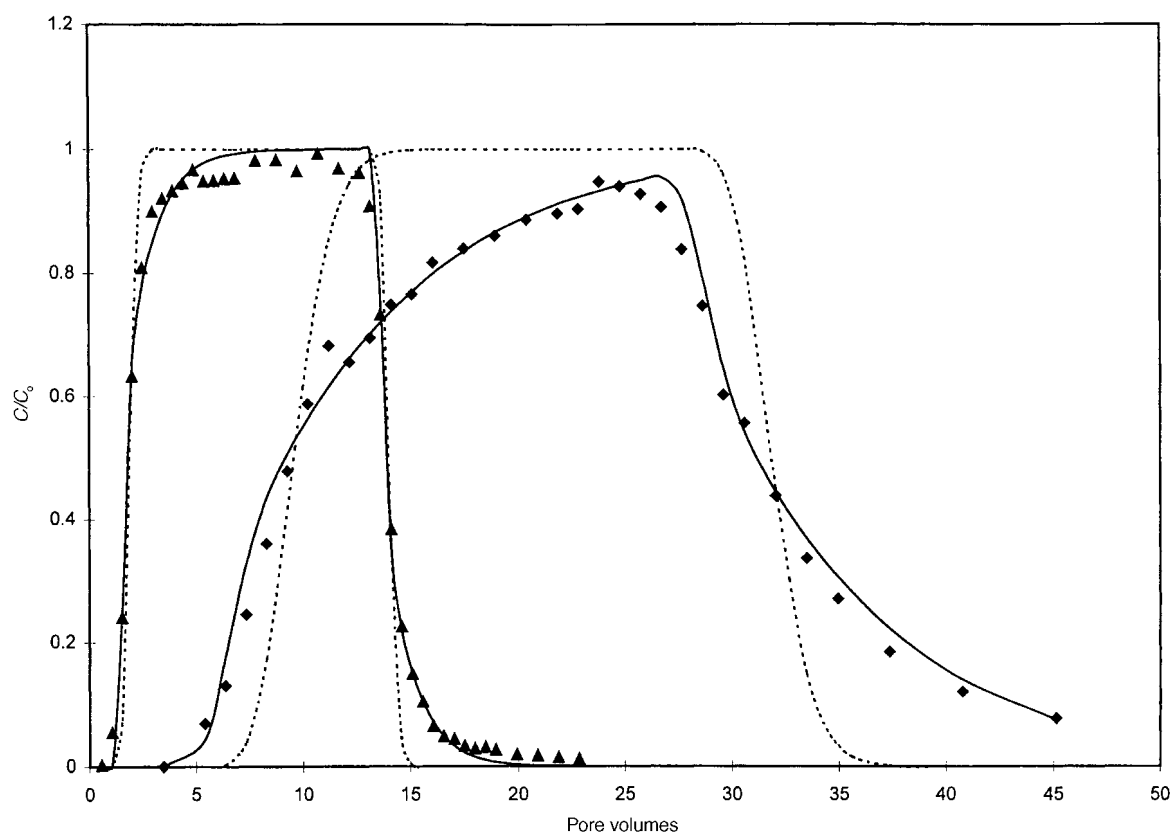


Figure 3. (◆) Vinclozolin and (▲) atrazine breakthrough curves for the Eustis soil. (---) Equilibrium model fit (—) two domain model fit.

the organic carbon of each geosorbent. The observation that the K_{oc} values for the one surface soil used in the study, Eustis, were lower than the K_{oc} values for the three sediments is consistent with a recent study where PAH K_{oc} values for sediments were about twice the values observed for soils.⁷

3.2 Column studies

3.2.1 Hydrodynamics

The BTCs for $^3\text{H}_2\text{O}$ and the four geosorbents (not shown) were all symmetric, and the data were described well by the advective-dispersive local equilibrium solute transport model. Such symmetry and equilibrium model fit is indicative of hydrodynamic equilibrium during transport; that is, that diffusional mass transfer of the $^3\text{H}_2\text{O}$ solute into and out of the microporous structure of the geosorbent occurred rapidly enough relative to solute resident times in the column to be at equilibrium with bulk water transport. Furthermore, the constancy of these BTCs indicated that the advective-dispersive transport characteristics of the columns did not change significantly over the duration of the experiments. Fitting the advective-dispersive local equilibrium solute-transport model to the $^3\text{H}_2\text{O}$ data yielded the Peclet numbers reported in Table 1. The Peclet numbers measured in these experiments were consistent with the low dispersion expected for well-packed, unaggregated sorbents, and are comparable to those measured by other researchers using similar column apparatus.^{3,8} These Peclet

numbers were then used in the two-domain model for simulating vinclozolin and atrazine transport through the columns.

3.2.2 Sorption and transport

The vinclozolin and atrazine BTCs for the Eustis soil (Fig 3) are representative of the BTCs obtained for the other geosorbents. As suggested by the batch studies, atrazine was more mobile than vinclozolin in the four geosorbents. While a tremendous amount of environmental transport and fate research has been reported for atrazine,^{9,10} the environmental fate literature on vinclozolin is relatively sparse.^{11,12} In two atrazine studies using surface soils with organic carbon contents ranging from 0.13 to 2.6%,^{13,14} and in a third study using the coarse silt fraction (OC=3.27%) of a sediment,¹⁵ K increased with geosorbent organic carbon content and K_{oc} values were similar to those in this study (Table 2). Comparing the K_{oc} values in Table 2 with those from a study using both experimentally measured vinclozolin K_{oc} values and values derived from HPLC data¹⁶ revealed that our data were in close agreement with the predicted sorption coefficients and less than the measured values by about a factor of two.

Most of the vinclozolin and atrazine BTCs exhibited some degree of asymmetry or 'tailing' (the slow approach to $C/C_0=1$ or 0) that is characteristic of non-equilibrium sorption during solute transport. The data in Fig 3 clearly illustrate this effect, and the only

exception to this pattern was the BTC of the atrazine-Lightwood Log creek sediment combination which yielded a very low K value and a symmetric BTC. The observed BTC asymmetry may be caused by several phenomena, the foremost of which are isotherm non-linearity, hydrodynamic non-equilibrium, and sorption non-equilibrium. Since isotherm linearity and hydrodynamic equilibrium were experimentally verified, sorption non-equilibrium may be assumed to be the source of the BTC asymmetry observed in our experiments. One of the important environmental consequences of sorption non-equilibrium is that it contributes to the dispersion of pesticide mass during transport events. This increased dispersion may result in more rapid transport of trace amounts of pesticides to ground-water than that predicted assuming sorption equilibrium. The persistence of pesticide residues in sediments may also be underestimated when assuming sorption equilibrium.

As observed in Fig 3, the equilibrium transport model provided poor fits for the vinclozolin and atrazine data. However, the two-domain model simulations provided good descriptions of the experimental data. It should be noted that the two-domain model has had its greatest success in describing non-equilibrium sorption at relatively short time scales.^{3,4,17} Therefore, it probably best describes pesticide sorption and transport within a few days of pesticide-geosorbent contact time. Such scenarios would include sorption and transport within several

days of application or within a similar time interval following a rainfall or irrigation event. It would not be appropriate to apply the two-domain model, for example, to describe desorptive vinclozolin or atrazine release from soil or sediment following long pesticide-geosorbent contact times. Desorption in these instances is often characterized by a very slow release of trace amounts of pesticide over long periods of time that are not described well by two-domain model simulations. In cases such as these, pesticide desorption and subsequent transport in water may be more successfully modeled using a distributed parameter approach,¹⁸ and this is fertile territory for further study.

3.2.3 Organic carbon effects on k_2

Given the range of geosorbent organic carbon contents used in this study (Table 1), it was possible to evaluate the effect of geosorbent organic carbon content on sorption kinetics. The effect of geosorbent organic carbon content on vinclozolin sorption kinetics is evident in Fig 4, where the vinclozolin BTCs clearly become more asymmetric as geosorbent organic carbon content increases. For clarity, only the front portions of the BTCs are shown in Fig 4. Also, evident in Fig 4 is the inadequacy of the equilibrium model for describing vinclozolin transport through the geosorbents. However, when slow sorption kinetics were accounted for with the two-domain non-equilibrium model, very good descriptions of the experimental data

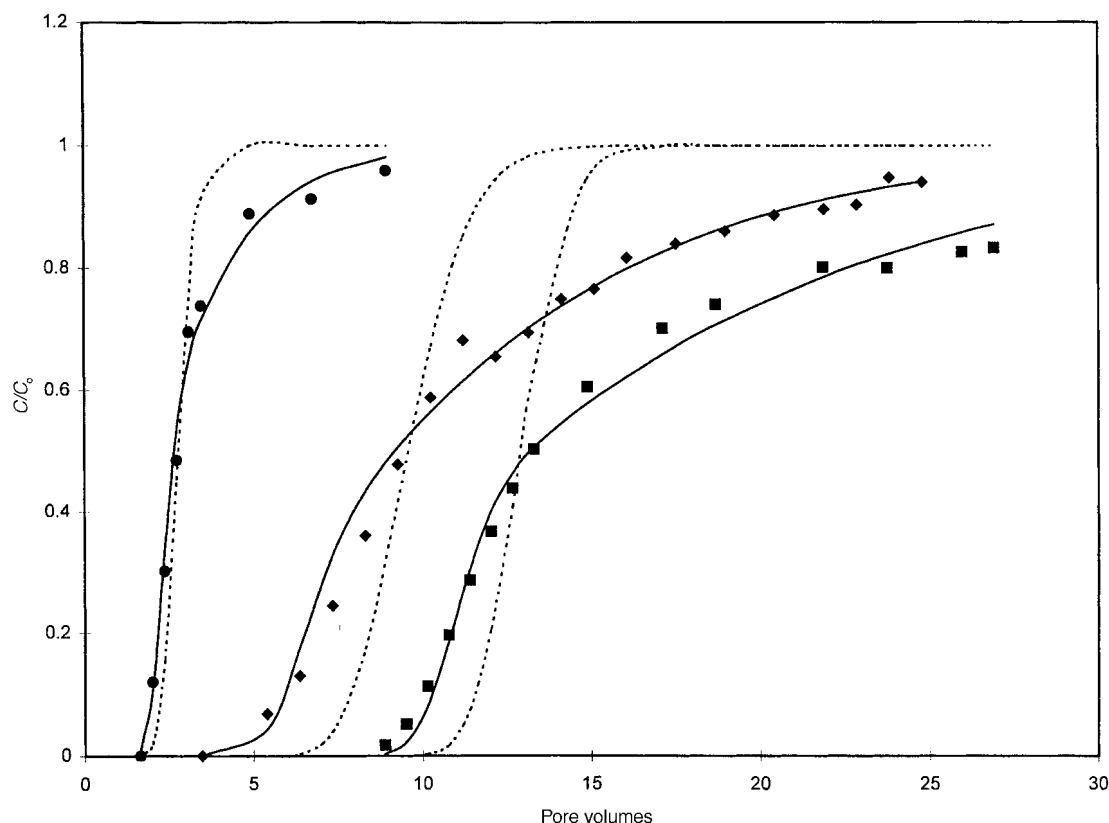


Figure 4. Vinclozolin breakthrough curves for (◆) Eustis soil and (■) Oconee and (●) Lightwood sediments. (---) Equilibrium model fit. (—) two-domain model fit.

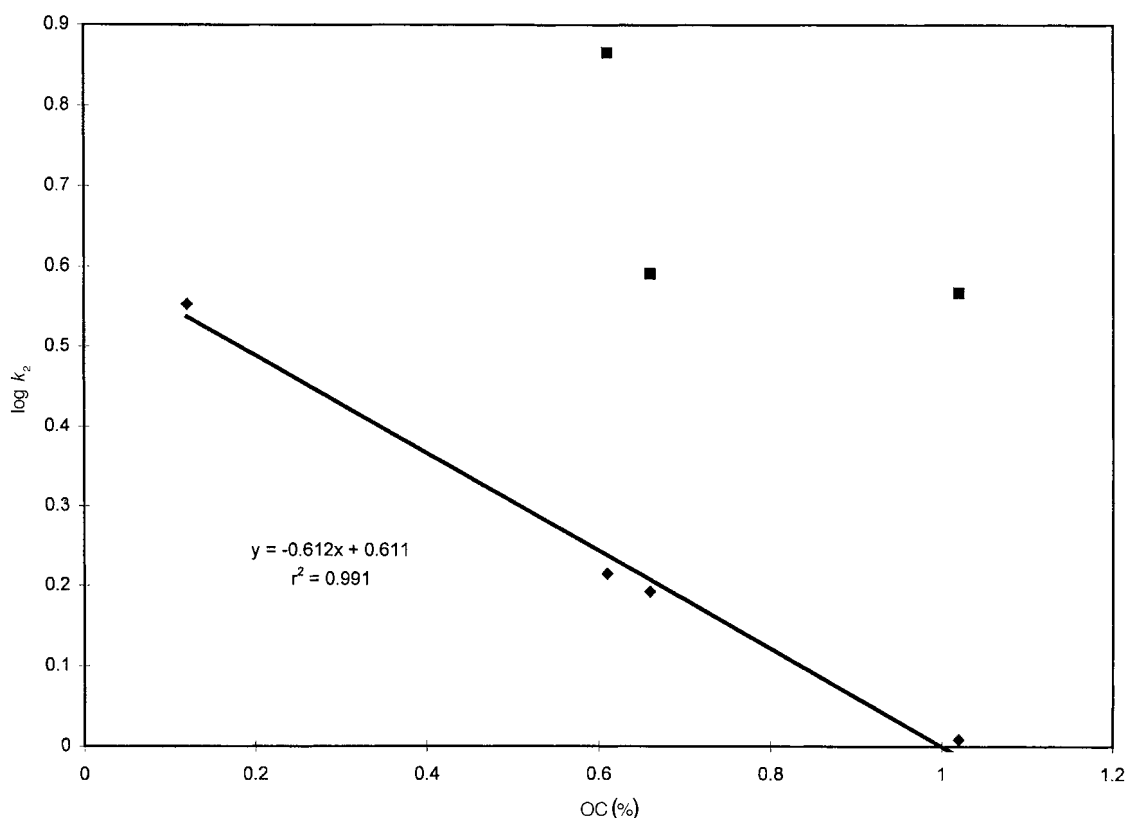


Figure 5. (◆) Vinclozolin and (■) atrazine desorption rate coefficients as a function of geosorbent organic carbon content.

were obtained again. Figure 5 shows the dependency of the desorption rate coefficient (k_2) on geosorbent organic carbon content. The dependency of k_2 on geosorbent organic carbon content for vinclozolin was strong ($r^2=0.991$). The relationship between k_2 and geosorbent organic carbon content was not as well defined for atrazine because k_2 could not be accurately determined for the atrazine-Lightwood Log creek sediment combination; however, there does appear to be a negative correlation between the two parameters.

The observed inverse relationship between k_2 and geosorbent organic carbon content supports the conceptual model proposed by this author² and others¹⁹ that non-equilibrium sorption is due mainly to slow diffusion within the organic carbon matrix. Longer pesticide diffusion path lengths through greater organic carbon mass will result in lower k_2 values as longer pesticide-geosorbent contact times are required to achieve pesticide access to all sorption domains within the geosorbent organic matter. Since many pesticide transport models and leaching algorithms assume sorption equilibrium, the accuracy of these predictive tools may decrease as soil and sediment organic carbon contents increase.

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